Advances in the Study of Geochemistry and Paleo-oceanography of the Co-rich Crust

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Abstract The current advances in the study of geochemistry and paleo-oceanography of the Co-rich crust are reviewed in this paper. We summarize the study of geochemistry of the Co-rich crust, discuss the diffusion of elements in the Co-rich crust and the exchange with ambient seawater. Besides, we discuss the effect of phosphatization and substrate rocks on the composition of the Co-rich crust. We also introduce the application of stable isotopes (including the stable isotopes of Pb, Nd, and Hf), radioactive isotopes (including the radioactive isotopes of Be, U and Th), and elements (including the major elements, minor elements and rare earth elements) to the study of paleo-oceanography of the Co-rich crust.

Keywords Co-rich crust, geochemistry, paleo-oceanography, advance

Previous studies on paleo-oceanography were often focused on the sediment core. However, the sediment core doesn't offer a long time scale because it deposites quickly, usually thousands of times quicker than the ferromanganese crust. Comparing with the long sediment core, ferromanganese crust is easier to get and the costs of sampling are lower. Besides, based on the geochemical studies, the Co-rich crust is less disturbed by the ambient environment and the interaction between crusts and seawater can almost be ignored. It acts as a closed system once it is formed. That's why Co-rich crust has become another focus of paleo-oceanography and marine scientists have paid more attention to it in recent years.

1 Summaries on the geochemical studies of Co-rich crusts

The Co-rich crust grows slowly on the substrate rock at a rate of several mm per Ma. It is a long-term record of mineralization environment, marine enviroment and global changes, for example, the changes of provenance, paleocirculation, paleo-redox potential of bottom seawater, paleoproductivity and paleoclimate, *etc.* These are often saved in the elemental and isotopic composition and other characteristics of the geochemistry of Co-rich crusts. Therefore, the elemental and isotopic composition in the Co-rich crust and the related geochemical characteristics should be known first before dating the crust and studying the history of paleo-oceanography. Besides, the geochemical behaviors of elements and isotopes in the crust also determine whether they can be used or not. Accordingly, the important precondition of the paleo-oceanographical study is to understand the geochemical behavior of the Co-rich crust and find the reliable tracer.

In recent years, studies on the source, composition and distribution of the elements in the Co-rich crust and the factors affecting these geochemical characteristics have been carried out. Most of these were concentrated on the material exchange with the ambient seawater and substrate, elemental

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diffusion and phosphatization effects during crusts' accretion. These studies establish the foundation for the application of stable and radioactive isotopes and elements to the paleo-oceanographical studies of Co-rich crusts.

1.1 Elemental diffusion in the Co-rich crust and exchange with ambient seawater

Henderson and Burton[1] calculated the effective elemental diffusion rates of U, Th, Li, Os, Sr, Be, Nd, Pb and Hf in the Co-rich crust (Table 1). The diffusion of Li, Os and Sr is too quick for us to record the composition of paleo-seawater accurately. Based on the chemical leach experiment, VonderHarr *et al.*[2] also proved that Sr in the Co-rich crust does exchange with the seawater. Diffusion of U is also quick, resulting in the growth rates induced by the depth profile of $^{234}U/^{238}U$ faster than those induced by ^{10}Be, $^{230}Th_{ex}$ dating. This is identical with Neff's results[3] that the exchange coefficient of U between the Co-rich crust and the ambient seawater is $5\times10^{-6}\ a^{-1}$ obtained from the discrepancy of the growth rates. As Th, Nd, Pb and Be are quite steady in the Co-rich crust, it is reliable to apply these elements to the dating and paleo-oceanographical studies of the Co-rich crust. Hf also diffuses to a certain extent, but David[4] thought the diffusion rate of Hf is much higher than actual since the used concentration of seawater was not correct[5]. If the correct concentration[6] is used, the diffusion rate will be at the same level as Be, which means Hf is also quite steady in the crust. The discussion above shows that many elements, especially particle-active elements, are pretty steady in the Co-rich crust and the diffusion can be ignored, which means the substance exchange with ambient seawater can be ignored.

Tab. 1 Effective diffusivities of some elements in the Co-rich crust[1]

Elements	Th	Nd	Pb	Be	Hf	U	Sr	Os	Li
Diffusion rate (cm^2/a)	2×10^{-12}	2×10^{-11}	3×10^{-11}	1×10^{-10}	3×10^{-8}	1×10^{-6}	2×10^{-5}	3×10^{-5}	2×10^{-4}

1.2 Influence of substrate rocks on the Co-rich crust composition

The Co-rich crust contacts not only with the ambient seawater but also with the substrate rocks at the bottom. This is different from the ferromanganese nodule, which contacts with sediment at the bottom. It is known that the pore water markedly affects the composition of ferromanganese nodule. However, since the early 1980s, studies on the Co-rich crust have always supposed that the substrate rocks don't influence the Co-rich crust composition[7]. This hypothesis wasn't validated until Hein and Morgan[8] approved it based on the studies on the chemical and mineral composition of both the Co-rich crust and the underlying substrate rocks and some other statistical analysis results. This is the only direct and detailed evaluation on the interaction between substrate rocks and the Co-rich crust so far.

1.3 Influence of phosphatization on the Co-rich crust composition

When the climate is steady and the circulation sluggish, the dissolved phosphorus derived from the intense chemical weathering accumulates in large quantities in the deep sea. When the Antarctic glaciation expands and the ocean circulation intensifies, the phosphorus-rich deep seawater would upwell because of the benthal topographhty and stay in the oxygen minimum zone (OMZ) temporarily. As OMZ expands, the O_2-poor and phosphorus-rich seawater would get to the slopes of seamounts where the crust is growing. That will further restrain the precipitate of the crust and the carbonate fluorapatite (CFA) will impregnate. From the late Eocene through Miocene, two major and possibly three minor episodes of phosphogenesis resulted in the phosphorite formation on equatorial Pacific seamounts. According to the crust age, the major event at 27-21Ma and the minor event at about 15Ma would result in the phosphatization of the crust.

Phosphatization distinctly affects the chemical and mineral composition of the Co-rich crust including major and minor elements and rare earth elements composition, *etc.*[8~10]. Under the influence of phosphatization, CFA impregnates the Co-rich crust and diagenetic remobilization and reorganization in the crust take place. There are controversies on whether phosphatization changes the composition of the steady isotope in the crust. Frank *et al.*[11] thought phosphatization has no effect on the composition of the steady isotopes of Pb and Nd in the Co-rich crust. Christensen *et al.*[12] also thought that phosphatization doesn't change the compostion of the steady isotope of Pb in the Co-rich crust. However, Ling *et al.*[13] thought phosphatization probably has some effect on the composition of the steady isotope of Pb in the Co-rich crust, but has no effect on the steady isotope of Nd. Lee *et al.*[14] thought that phosphatization doesn't alter the history of Hf isotopic composition. Therefore, more attention must be paid to the application of a variety of geochemical characteristics of the old part phosphatization crust to the studies of paleo-oceanography.

2 Progresses in paleo-oceanography studies of the Co-rich crust

Based on the geochemical characteristics of the crust, environmental characteristics of mineralization such as the chemical composition of the ambient seawater can be got directly. A series of studies have been made to get the distribution pictures and time series of the isotopes of Pb, Nd, Os, Hf, Be, U and Th in the Pacific, Indian and Atlantic Oceans. Besides, other studies also show the redox status of the ambient seawater and sediment. The provenance and the movement of water mass may be reflected from the chemical compositions and characteristics of the ambient seawater during the crust growth. The changes of the mineralization environment, paleo-ocean environment, the pattern of ocean circulation, and the interaction between these changes with the changes of paleogeography and paleoclimate can be further studied, thereby, linking the growth of the crust with the global change.

2.1 Application of stable isotopes in the Co-rich crusts to paleo-oceanography

The distribution of isotopes of Pb and Nd in deep seawater in the past 60Ma was controlled by: (a) variations in the oceanic mixing patterns and flow paths of water masses with distinct isotopic signatures related to major paleogeographic changes and (b) variability of supply rates or provenance of detrital material delivered to the ocean, which was linked to the climate change (glaciations) or major tectonic uplift[11]. The major paleogeographic change was closure of the Panama isthmus in 3~5Ma BP, the climate change was the start of the Northern Hemisphere glaciation (NHG), and the major tectonic uplift refers to the uplift of the Himalayas. Consequently, correlative information can be got from the studies of isotopes of Pb and Nd in the crust. These studies show that the closure of Panama isthmus and the start of NHG established the modern pattern of the ocean circulation[13, 15~17]. Further, the changes of the pattern of ocean circulation lead to the distinct changes of the composition of isotopes of Pb and Nd [18~20] and the source of material[19, 21~23] in the deep water. The studies on crusts in Southwest and Central Indian Ocean indicate that the Himalayan erosion contributes little to the composition of the deep seawater of the Indian Ocean in the past 20 Ma[18], while the input of Himalayan errosion can be distinguished from the crust located in North Indian Ocean, and maybe the input was only limited to a small scale. However, other events like the outcrop of the Greenland-Scotland ridge may probably affect the input of Pb and Nd to the ocean[21].

The isotope of Hf can also be used in the studies on variations of prevenance of material, paleo-climate, paleo-ocean circulation and paleo-georgraphy. Godfrey *et al.*[25] thought that the isotope of Hf in the crusts could be used to determine the source of Hf, probably Fe and Mn. The shifts in the composition of Hf isotope in North Atlantic crust may have been caused by change of the erosion intensity as glaciation progressed in the northern hemisphere, while those shifts of Hf isotopic composition in the crust of Indian Ocean may have been caused by a short-term increase in Himalayan erosion and alternatively by the expanding influence of NADW into the Mid-Indian Basin via circum-Antarctic deep water (CDW) or a reduction of Pacific flow through the Indonesian gateway[26]. Lee *et al.*[14] found that the Hf isotopic composition in the Central Pacific deep water relates closely to the changes in paleo-geography and paleo-ocean circulation. David *et al.*[4] have also proved that the Hf isotope could be used as the tracer of source of elements and water masses.

2.2 Application of radioactive isotopes in the Co-rich crusts to paleo-oceanography

Ratio of $^{10}Be/^{9}Be$ is a good tracer of water mass movement and paleo-flux[27]. Von Blankenburg and O'Nions[28] used the ratio to trace the change in the intensity of NADW and the source of stable isotopes of Nd and Pb. Chabaux[29] thought that the ratio of Th/U and the initial activity ratio of Th related to the changes of ocean circulation in the past 150ka. Eisenhauer *et al.*[30] found the interaction between the growth of crust and the changes of climate in the late Quaternary climate change through the elements input in the water column based on the study of the depth profiles of ^{230}Th in crusts. Huh and Ku[31] studied the change in the intensity of aeolian dust related to the paleo-climate such as NHG through the distribution of ^{232}Th in crusts and nodules.

2.3 Application of elements in the Co-rich crusts to paleo-oceanography

Changes in the elemental compositions of the crusts also reflect the variation of paleo-climate and paleo-ocean environment. Segl *et al.*[32] found that the changes of the chemical composition of the crust happened at the same time as the paleo-climate events from the late Tertiary to the Quaternary. Halbach and Puteanus[33] found that the changes in the composition of the crust reflect the variation of the paleo-ocean environment, including dissolution rate of carbonate, the bottom current and the biological productivity etc. Based on the studies of the chemical composition of seamount crust in the Central Indian Ocean, Banakar and Hein[34] drew the conclusion that the growth of crusts was affected by the changes of carbonate compensation depth (CCD), depth of crust formation, early Eocene productivity, instability of substrate rock, parttern of ocean circulation and oxygenation of Indian Ocean deep water. Hein *et al.*[35] found that changes in the chemical composition of the crust was related to the changes of the paleo-ocean circulation and development of icecap at the poles in the study of the crusts of the Central Pacific Ocean. Besides, the climate change forced by the Earth motion has also affected the composition of crusts.

2.4 Progresses in the paleo-oceanographic study of the Co-rich crusts

Paleo-oceanographic studies of the Co-rich crust have also been carried out in China. Xu Dong Yu[36] summarized the variations of paleo-oceanographic environment of Central Pacific Seamount areas where crusts were growing. Liang Hongfeng *et al.*[37] thought that the growth of the crust located at Jianfeng Seamount in the South China Sea was controlled by the particular marine environment in the

South China Sea and maybe was influenced by the hydrothermal activity from the benthal volcanoes. He also drew the conclusion that the growth of crusts was influenced by the input of material and paleo-oceanographic condition based on the comparison study on the geochemical behaviors of elements in the crust of Central Pacific Ocean Seamount, the Philippine sea basin and the South China Sea[38]. The relation of the geochemical characteristics of major elements to the paleao-oceanographic environment in Western Pacific has also been discussed by Pan Jiahua and Liu Shuqin[39]. The result of Xu Dongyu[40] showed that the paleo-oceanographic environment and events such as Antarctic Bottom Water, upwelling, biological productivity, deposit discontinuity influenced and controlled the formation and distribution of polymetallic nodule, the Co-rich crust and seamount apatite. Further studies should be focused on the complete and accurate explanation of the record of mineralization environment in the crusts, so as to uncover the mechanism of mineralization and establish the pattern of mineralization.

3 Conclusions

Studies on the geochemistry in the Co-rich crusts are reviewed in our article. We focus on the exchange between the crust and seawater and substrate rock, the elemental diffusion in the crust and the effect of phosphatization on the crust, and so on. At the same time, the progresses in paleo-oceanographic studies of the Co-rich crust, including the use of isotopes, elements, are introduced.

Presently, there is still not a whole picture of the geochemical behavior of the isotopes and elements in the Co-rich crust. This limits the application of these isotopes and elements in the paleocaeagraphic studies and counteracts the development of paleo-oceanographic study. More and more will be known about the geochemical behavior and distribution characteristics of the elements and isotopes in the Co-rich crust following the improvement of the analysis methods. This will then promote the further development of paleo-oceanographic studies.

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